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Process for the production of a water-soluble polymer dispersion.

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㉓ Proprietor: KYORITSU YUKI CO. LTD.
13-15 Ginza 7-chome
Chuo-ku Tokyo (JP)

㉔ Inventor: Takeda, Hisao
4-2923-26, Iriya
Zama-shi Kanagawa-ken (JP)
Inventor: Kawano, Mutsumi
1301-6, Kagawa
Chigasaki-shi Kanagawa-ken (JP)

㉕ Representative: Brown, John David et al
FORRESTER & BOEHMERT Widenmayerstrasse
4/1
D-8000 München 22 (DE)

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Courier Press, Leamington Spa, England.

Description

This invention relates to a process for the production of a dispersion of a water-soluble polymer, which polymers are widely used, for example as flocculating agents for waste water treatment, dehydrating agents, chemicals for use in paper making processes, dispersion stabilizers for various suspensions, soil improvers and so on.

Heretofore, as processes for the production of water-soluble polymers used in such fields as those described above, there have been proposed, for example, stationary polymerization in an aqueous solution, water-in-oil type emulsion polymerization (Japanese Patent Application Laid-open No. 102388/1979), and suspension polymerization in a hydrophobic solvent (Japanese Patent Application Laid-open No. 69196/1979). Furthermore, Japanese Patent Application Laid-open No. 70489/1975 discloses precipitation polymerization in an aqueous solution of a salt and Japanese Patent Publication No. 14907/1971 discloses polymerization in an aqueous solution mainly comprising acrylic acid at a low pH and containing a salt.

In stationary polymerization in an aqueous solution, because the polymerization is conducted at a monomer concentration of 10% by weight or more in order to obtain a polymer of a high molecular weight, the product is in hydrated gel form and hence cannot be easily dissolved as such and therefore it is necessary either to dilute and sell the same as a flowable, low concentration product or to dry it to a powder. Where it is put on the market at a low concentration, the transport cost is increased, whereas the heat energy required for drying to a powder is great. Also, three-dimensional crosslinking is brought about by heating and an undesirable water-insoluble part is produced.

The water-in-oil type emulsion is inflammable and also has the disadvantage that valuable organic solvents are wastefully consumed. With the suspension polymerization in a hydrophobic solvent, because inflammable substances such as cyclohexane and toluene are used, there is the disadvantage that an enormous cost is required for the production apparatus.

Although precipitation polymerization in an aqueous salt solution is low in equipment cost and is a good process, it has the drawback that the polymer formed tends to stick together and grow into a mass, rendering handling very difficult.

In the process described in Japanese Patent Publication No. 14907/1971, the dispersion is stable only under acidic conditions, and when the carboxyl groups are dissociated, it turns to a gel. However, since an anionic flocculating agent generally manifests its effect by dissociating the carboxyl groups and extending the polymer chain, the acidic flocculating agent does not manifest a satisfactory effect if not neutralized before use except in the case where it is used in an alkaline solution at a high pH. Furthermore, it is difficult using this process to produce a polymer flocculating agent having a degree of anionization of 15 mole% or less which is most effective as a flocculating agent.

FR—A—2251367 discloses the production of a polymer dispersion by a process whereby a water-soluble monomer is dissolved in an organic phase, which organic phase comprises a suspension of droplets in an aqueous salt solution. The salt is present in the aqueous phase to prevent the water-soluble monomer from dissolving in the aqueous phase. The monomer is cross-linked in the organic phase to produce a dispersion of microfine, substantially spherical, polymer beads in the aqueous phase.

It is an object of the present invention to enable the provision of a process for the preparation of a water-soluble polymer dispersion whereby the above disadvantages may be overcome or at least mitigated.

This invention accordingly provides a method of obtaining a dispersion of a water-soluble polymer by dissolving a monomer in an aqueous salt solution and conducting polymerization while depositing the polymer as fine particles in the presence of a dispersant. The aqueous salt solution is required to dissolve the monomer and precipitate the polymer.

As the dispersant, a polymer electrolyte and/or a polyol soluble in an aqueous salt solution is/are effective.

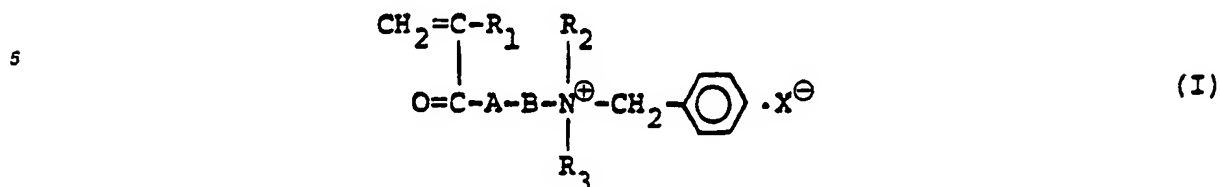
Where the deposited polymer is an anionic or cationic polymer electrolyte, the polymer electrolyte used as the dispersant is required to have charges of the same kind as the deposited polymer.

The amount of the dispersant used should be 0.1% by weight or more based on the aqueous salt solution. The polymer dispersion obtained is of low viscosity and has good flowability, and thus is convenient for transport by pumping or dissolution. Since no organic solvent is used, there is no risk of inflammability and also the cost is low.

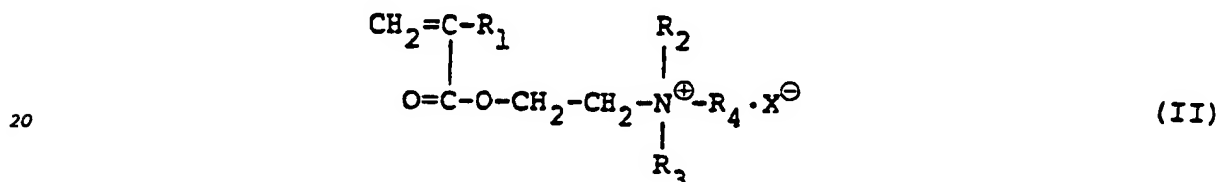
The invention relates in a preferred aspect to a process for the production of an easily flowable water-soluble polymer dispersion which comprises polymerizing an acrylic water-soluble monomer (A) while depositing the polymer with stirring in an aqueous salt solution, in the presence of a dispersant (B).

Examples of the acrylic water-soluble monomer (A) include (meth)acrylamide, N,N-dimethylacrylamide, (meth)acrylic acid alkali metal salts, 2-acrylamido-2-methylpropanesulfonic acid alkali

metal salts, cationic monomers represented by the following formulae (I) and (II):



wherein R_1 is H or CH_3 ; R_2 and R_3 are each an alkyl group of 1—3 carbon atoms; A is an oxygen atom or NH; B is an alkylene group of 2—4 carbon atoms or a hydroxypropylene group; and X^- is an anionic counterion,



wherein R_1 is H or CH_3 ; R_2 and R_3 are each an alkyl group of 1—3 carbon atoms; R_4 is H or an alkyl group or alkanol group of 1—3 carbon atoms; and X^- is an anionic counterion, and the like.

While one or a combination of two or more of the above-described monomers may be selected, since the polymerization is conducted while depositing the polymer, there is one requisite that the formed polymer of the monomer (A) not be soluble in the aqueous salt solution. Although as regards the nonionic monomers such as acrylamide etc., this invention can be carried out even in the case of homopolymerization, the ionic monomers other than the monomers of the formula (I) cannot be homopolymerized since the polymers are soluble in the aqueous salt solution.

For that reason, for the ionic monomers other than those of the formula (I), copolymerization with anionic monomers such as acrylamide etc. is preferred and the amount is suitably 15 mole% or less.

As regards the cationic monomers of the formula (I), a highly hydrophobic benzyl group is attached to the amino group, and, as a result, the monomers of the formula (I) do not dissolve in the aqueous salt solution even in homopolymerization and may be used at proportions in a wide range.

Further, since this invention relates to a process for the production of a water-soluble polymer, as long as the polymer of the water-soluble monomer (A) is water soluble, the combination of the monomers is not restricted to those described above. For example, a monomer having solubility in water to some degree such as acrylonitrile etc. may also be used as long as the copolymer with the water-soluble monomer (A) is water-soluble.

There is a requirement that the aqueous salt solution which is a dispersion medium for the polymerization should not dissolve the polymerization product. Representative salts include sodium sulfate, ammonium sulfate, magnesium sulfate, aluminium sulfate, sodium chloride, sodium dihydrogenphosphate, diammonium hydrogenphosphate, dipotassium hydrogenphosphate and mixtures of two or more of these salts. Apart from these salts, those others which do not dissolve the polymerization product are also encompassed in the scope of this invention.

While the concentration of the aqueous salt solution is not particularly restricted and varies depending on the molar ratio of the ionic monomers and the salt used, the range of from 15% by weight to the upper limit of solubility is generally preferred. Further, it is also possible to reduce the viscosity of the dispersion by further adding the salt in the range of solubility to the dispersion after polymerization.

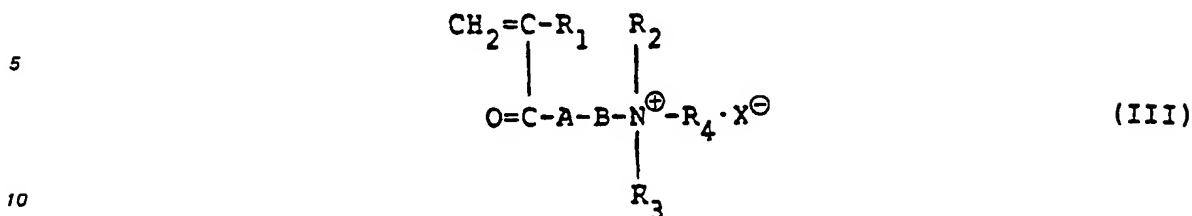
The amount of the dispersant used is preferably 0.1% by weight or more based on the aqueous salt solution, and with less than 0.1%, the formed polymer cannot be obtained in a dispersed form and sticks to each other to grow into a bigger mass, and thus it is not preferred. Examples of the polyol to be co-present as the dispersant on polymerization include ethylene glycol, propylene glycol, glycerin, pentaerythritol, sorbitol, and polyethylene glycol, polypropylene glycol etc. of a molecular weight of up to 600, but are not restricted thereto.

Further, the polymer electrolyte to be co-present as the dispersant on polymerization is not particularly restricted as long as it is soluble in the aqueous salt solution used for polymerization.

Where the formed polymer is nonionic like polyacrylamide, either cationic polymer electrolyte or anionic polymer electrolyte may be used, but where the formed polymer is anionic, then an anionic polymer electrolyte is preferred and where cationic, then a cationic polymer electrolyte is preferred.

The anionic polymer electrolyte is preferably a polymer of an acrylic acid alkali metal salt, a 2-acrylamido-2-methylpropanesulfonic acid alkali metal salt, or a copolymer containing at least 30 mole% thereof, and the cationic polymer electrolyte is preferably a polymer of one or more cationic monomers of

the following formula (III) or a copolymer containing 20 mole% or more thereof:



wherein R_1 is H or CH_3 ; R_2 and R_3 are each an alkyl group of 1—2 carbon atoms; R_4 is H or an alkyl group of 1—2 carbon atoms; A is an oxygen atom or NH; B is an alkylene group of 2—4 carbon atoms or a hydroxypropylene group; and X^- is an anionic counterion.

While representative examples of the cationic monomers of the formula (III) include dimethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, dimethylaminohydropropyl (meth)acrylate and those obtained by quaternizing those with methyl chloride, dimethylsulfuric acid etc., monomers satisfying the formula (III) may all be used.

The polymerizing method is outlined below, and more detail will be later described in the examples.

A predetermined acrylic water-soluble monomer (A) is charged into an aqueous salt solution in which a dispersant has been already dissolved, oxygen is displaced by nitrogen gas, then a polymerization initiator is added, and the polymerization is started with stirring. When the polymerization reaches completion, polymer particles of a particle diameter of 1mm or less may be obtained in a dispersed form. The monomer concentration at that time is in the range of 5 parts by weight or more based on 100 parts by weight of the aqueous salt solution, and if it is less than 5 parts by weight, there is no superiority to aqueous solution polymerization. On the other hand, the upper limit is where the flowability of the product is lost.

The polymerization temperature varies depending on the kind of polymerization initiator and is not particularly restricted as long as the initiator functions well. Further, the polymerization initiator is not particularly restricted, and, for example, the conventionally employed redox type, azo type etc. may be used.

Examples

This invention is more particularly described by the following examples, but it should be understood that this invention is not limited to these examples.

Example 1

To a 1-litre five-necked separable flask equipped with a stirrer, a thermometer, a reflux condenser and a nitrogen inlet tube were added 2.5 g of homopolymer of acryloyloxyethyltrimethylammonium chloride, 112.5 g of ammonium sulfate and 335 g of deionized water and dissolved, then 35.1 g (90 mole%) of acrylamide and 14.9 g (10 mole%) of acryloyloxyethyldimethylbenzylammonium chloride were charged, then heated to 50°C and the air inside was displaced by nitrogen.

One g of a 1% aqueous solution of 2,2'-azobis(2-amidinopropane) hydrochloride was added thereto as a polymerization initiator, and the polymerization was conducted with stirring at 50°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

The viscosity of this product was 500 cp at 25°C, and the viscosity of this polymer at 0.5% in 1 N sodium chloride aqueous solution was 22.0 cp.

Example 2

To the separable flask used in Example 1 were added 3.8 g of a copolymer obtained by polymerizing acrylamide and acryloyloxyethyltrimethylammonium chloride at a molar ratio of 75:25, 42.5 g of aluminum sulfate, 42.5 g of sodium sulfate and 336.2 g of deionized water and dissolved, then 52.7 g (90 mole%) of acrylamide and 22.3 g (10 mole%) of acryloyloxyethyldimethylbenzylammonium chloride were charged, then heated to 50°C and the air inside was displaced by nitrogen.

1.5 g of a 1% aqueous solution of 2,2'-azobis(2-amidinopropane) hydrochloride was added thereto, and the polymerization was conducted with stirring at 50°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

The viscosity of this product was 2400 cp at 25°C, and the viscosity of this polymer at 0.5% in 1 N sodium chloride aqueous solution was 32.0 cp.

Example 3

To a 1-litre five-necked separable flask equipped with a stirrer, a thermometer, a reflux condenser, and a nitrogen inlet tube and a dropping funnel were added 1.3 g of a homopolymer of methacryloyloxyethyltrimethylammonium chloride, 90 g of sodium sulfate and 318.7 g of deionized water and dissolved, then heated to 50°C and the air inside was displaced by nitrogen. Thereafter, that obtained by mixing and

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dissolving 34.6 g (90 mole%) of acrylamide, 15.4 g (10 mole%) of methacryloyloxyethyltrimethylammonium chloride, 40 g of deionized water and 0.05 g of 2,2'-azobis(2-amidinopropane) hydrochloride was put into the dropping funnel, and gradually added dropwise to the aqueous salt solution with stirring. By polymerizing at 50°C for 10 hours, a polymer was obtained in the form of fine particles dispersed in the aqueous salt solution.

The viscosity of this product was 1080 cp at 25°C, and the viscosity of the polymer at 0.5% in 1 N sodium chloride aqueous solution was 20.0 cp.

Example 4

To the separable flask used in Example 1 were added 3.8 g of a copolymer obtained by polymerizing acrylamide and methacryloyloxyethyltrimethylammonium chloride at a molar ratio of 50:50, 127.5 g of ammonium sulfate and 293.7 g of deionized water and dissolved, then 30.0 g (70 mole%) of acrylamide, 12.4 g (10 mole%) of dimethylaminoethyl methacrylate sulfate and 32.6 g (20 mole%) of acryloyloxyethyl-dimethylbenzylammonium chloride were charged thereinto, heated to 40°C and the air inside was displaced by nitrogen.

0.38 g of a 10% aqueous solution of ammonium persulfate and 0.38 g of a 10% aqueous solution of sodium hydrogensulfite were added thereto, and the polymerization was conducted with stirring at 40°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

The viscosity of this product was 2820 cp at 25°C, and the viscosity of the polymer at 0.5% in 1 N sodium sulfate aqueous solution was 17.0 cp.

Example 5

To the separable flask used in Example 1 were added 10 g of a homopolymer of dimethylaminoethyl methacrylate sulfate, 100 g of sodium chloride and 290 g of deionized water and dissolved, then 32.9 g (65 mole%) of acrylamide and 67.1 g (35 mole%) of acryloyloxyethyltrimethylammonium chloride were charged thereinto, heated to 50°C, and the air inside was displaced by nitrogen.

0.5 g of a 10% aqueous solution of 2,2'-azobis(2-amidinopropane) hydrochloride and 0.5 g of a 10% aqueous solution of sodium hydrogensulfite were added thereto, and the polymerization was conducted with stirring at 50°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

The viscosity of this product was 1920 cp at 25°C, and the viscosity of the polymer at 0.5% in a 1 N sodium sulfate aqueous solution was 18.0 cp.

Example 6

To the separable flask used in Example 1 were added 6.3 g of a homopolymer of acryloyloxyethyl-trimethylammonium chloride, 131.3 g of ammonium sulfate and 237.4 g of deionized water and dissolved, then 54.4 g (50 mole%) of methacryloyloxyethyltrimethylammonium chloride and 70.6 g (50 mole%) of acryloyloxyethyltrimethylbenzylammonium chloride were charged thereinto, heated to 50°C, and the air inside was displaced by nitrogen.

1.3 g of a 10% aqueous solution of 2,2'-azobis(2-amidinopropane) hydrochloride was added thereto, and the polymerization was conducted with stirring at 50°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

The viscosity of this product was 2120 cp at 25°C, and the viscosity of the polymer at 0.5% in a 1 N sodium sulfate aqueous solution was 10.3 cp.

Example 7

To the separable flask used in Example 1 were added 5.0 g of methacryloyloxyethyltrimethylammonium chloride, 100 g of magnesium sulfate and 295 g of deionized water and dissolved, then 100 g of methacryloyloxyethyltrimethylbenzylammonium chloride was charged thereinto, heated to 50°C, and the air inside was displaced by nitrogen.

1.0 g of a 10% aqueous solution of 2,2'-azobis(2-amidinopropane) hydrochloride was added thereto, and the polymerization was conducted with stirring at 50°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

The viscosity of this product was 1080 cp at 25°C, and the viscosity of the polymer at 0.5% in a 1 N sodium sulfate aqueous solution was 14.0 cp.

Example 8

To the separable flask used in Example 3 were added 8.8 g of a copolymer obtained polymerizing acrylamide and acryloyloxyethyltrimethylammonium at a molar ratio of 40:60, 113.8 g of sodium dihydrogenphosphate and 158.6 g of deionized water and dissolved, heated to 50°C, and the air inside was displaced by nitrogen. Thereafter, that obtained by mixing and dissolving 175 g of acryloyloxyethyl-dimethylammonium chloride, 43.8 g of deionized water and 0.18 g of 2,2'-azobis(2-amidinopropane) hydrochloride was placed in a dropping funnel, and gradually added dropwise to the aqueous salt solution with stirring. The polymerization was conducted at 50°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

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The viscosity of this product was 460 cp at 25°C, and the viscosity of the polymer at 0.5% in a 1 N sodium sulfate aqueous solution was 13.5 cp.

Example 9

5 To the separable flask used in Example 1 were added 10 g of homopolymer of methacrylamidopropyl-trimethylammonium chloride, 120 g of ammonium sulfate and 270 g of deionized water and dissolved, 100 g of acrylamidopropyl-dimethylbenzylammonium chloride was charged thereinto, then heated to 50°C and the air inside was displaced by nitrogen.

1.0 g of a 10% aqueous solution of 2,2'-azobis(2-amidinopropane) hydrochloride was added thereto, and the polymerization was conducted with stirring at 50°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

The viscosity of this product was 960 cp at 25°C, and the viscosity of the polymer at 0.5% in a 1 N sodium sulfate aqueous solution was 15.0 cp.

Example 10

15 Into the separable flask used in Example 1 were charged 75 g of acrylamide, 106.3 g of ammonium sulfate, 7.5 g of ethylene glycol and 311.2 g of deionized water, heated to 45°C and the air inside was displaced by nitrogen.

2.3 g of a 1% aqueous solution of 2,2'-azobis(2-amidinopropane) hydrochloride was added thereto as a polymerization initiator, and the polymerization was conducted with stirring at 45°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

The viscosity of this product was 2060 cp at 25°C, and the viscosity of the polymer at 0.5% in 1 N sodium chloride aqueous solution was 30 cp.

Example 11

25 Into the separable flask used in Example 1 were charged 75 g of acrylamide, 50 g of ammonium sulfate, 25 g of diammonium hydrogenphosphate, 3.8 g of glycerin and 296.2 g of deionized water, heated to 40°C and the air inside was displaced by nitrogen.

0.75 g of a 1% aqueous solution of ammonium persulfate and 0.75 g of a 1% aqueous solution of sodium hydrogensulfite were added thereto, and the polymerization was conducted with stirring at 40°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous solution.

The viscosity of this dispersion was 8400 cp at 25°C, and the viscosity of the polymer at 0.5% in 1 N sodium chloride aqueous solution was 70.2 cp.

When 50 g of diammonium hydrogenphosphate was further added to this dispersion, the viscosity was reduced to 350 cp.

Example 12

40 Into the separable flask used in Example 1 were charged 43.6 g (90 mole%) of acrylamide, 6.4 g (10 mole%) of sodium acrylate, 112.5 g of ammonium sulfate, 2.5 g of pentaerythritol and 335 g of deionized water, heated to 40°C, and the air inside was displaced by nitrogen.

1 g of a 1% aqueous solution of ammonium persulfate and 1 g of a 1% aqueous solution of sodium hydrogensulfite were added thereto, and the polymerization was conducted with stirring at 40°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

The viscosity of this product was 1830 cp at 25°C, and the viscosity of the polymer at 0.5% in 1 N sodium chloride aqueous solution was 25.5 cp.

Example 13

50 Into the separable flask used in Example 1 were charged 51.5 g (90 mole%) of acrylamide, 23.5 g (10 mole%) of sodium 2-acrylamido-2-methylpropanesulfonate, 106.3 g of ammonium sulfate, 3.8 g of sorbitol, 3.8 g of propylene glycol and 311.1 g of deionized water, heated to 45°C and the air inside was displaced by nitrogen.

3.8 g of a 1% aqueous solution of 2,2'-azobis(2-amidinopropane) hydrochloride was added thereto, and the polymerization was added thereto, and the polymerization was conducted with stirring at 45°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

55 The viscosity of this product was 910 cp at 25°C, and the viscosity of the polymer at 0.5% in 1 N sodium chloride aqueous solution was 40.7 cp.

Example 14

60 Into the separable flask used in Example 1 were charged 57.6 g (90 mole%) of acrylamide, 4.2 g (5 mole%) of sodium acrylate, 13.2 g (5 mole%) of sodium 2-acrylamido-2-methylpropanesulfonate, 63.8 g of ammonium sulfate, 42.5 g of sodium chloride, 7.5 g of polyethylene glycol #400 and 311.2 g of deionized water, heated to 45°C and the air inside was displaced by nitrogen.

2.3 g of a 1% aqueous solution of ammonium persulfate and 2.3 g of a 1% aqueous solution of sodium hydrogensulfite were added thereto, and the polymerization was conducted with stirring at 45°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

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The viscosity of this product was 1200 cp at 25°C, and the viscosity of the polymer at 0.5% in 1 N sodium chloride aqueous solution was 35.1 cp.

Example 15

5 Into the separable flask used in Example 1 were charged 52.7 g (90 mole%) of acrylamide, 22.3 g (10 mole%) of acryloyloxyethyltrimethylammonium chloride, 51 g of aluminum sulfate, 34 g of sodium sulfate, 3.8 g of glycerin and 336.2 g of deionized water, heated to 45°C and the air inside was displaced by nitrogen.

1.5 g of a 1% aqueous solution of 2,2'-azobis(2-amidinopropane) hydrochloride was added, and the
10 polymerization was conducted with stirring at 45°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

The viscosity of this product was 2100 cp at 25°C, and the viscosity of the polymer at 0.5% in 1 N sodium chloride aqueous solution was 40.3 cp.

Example 16

15 Into the separable flask used in Example 1 were charged 35.3 g (65 mole%) of acrylamide, 45.4 g (22 mole%) of acryloyloxyethyltrimethylammonium chloride, 19.3 g (13 mole%) of acryloyloxyethyltrimethylammonium chloride, 68.8 g of ammonium sulfate, 2.5 g of ethylene glycol, 2.5 g of polyethylene glycol # 200 and 270 g of deionized water, heated to 45°C and the air inside was displaced by nitrogen.

20 2 g of a 1% aqueous solution of 2,2'-azobis(2-amidinopropane) hydrochloride was added thereto, and the polymerization was conducted with stirring at 45°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution. The viscosity of this dispersion was 2500 cp at 25°C, and the viscosity of the polymer at 0.5% in a 3% sodium sulfate aqueous solution was 50.6 cp.

When 56.2 g of diammonium hydrogenphosphate was further added to this dispersion, the viscosity
25 was reduced to 390 cp.

Example 17

Into the separable flask used in Example 1 were charged 56.6 g (90 mole%) of acrylamide, 18.4 g (10 mole%) of methacryloyloxyethyltrimethylammonium chloride, 51 g of ammonium sulfate, 34 g of
30 diammonium hydrogenphosphate, 2.3 g of glycerin, 1.5 g of ethylene glycol and 336.2 g of deionized water, heated to 50°C, and the air inside was displaced by nitrogen.

1.5 g of a 1% aqueous solution of 2,2'-azobis(2-amidinopropane) hydrochloride was added thereto, and the polymerization was conducted with stirring at 50°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

35 The viscosity of this product was 3510 cp at 25°C, and the viscosity of the polymer at 0.5% in 1 N sodium chloride aqueous solution was 15.1 cp.

It is also possible to use a polymer electrolyte soluble in a aqueous salt solution in combination with a polyol. Such examples are given as Examples 18 and 19.

Example 18

40 Into the separable flask used in Example 1 were added 3.8 g of a homopolymer of sodium acrylate (the viscosity of its aqueous solution having a pure content of 0.5% being 10 cp at 25°C), 50 g of ammonium sulfate, 25 g of diammonium hydrogenphosphate, 3.8 g of propylene glycol and 292.4 g of deionized water and dissolved, 75 g of acrylamide was added thereto, heated to 45°C, and the air inside was displaced by
45 nitrogen.

2.3 g of a 1% aqueous solution of ammonium persulfate and 2.3 g of a 1% aqueous solution of sodium hydrogensulfite were added thereto, and the polymerization was conducted with stirring at 45°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution. The viscosity of this dispersion was 7200 cp at 25°C, and the viscosity of the polymer at 0.5% in 1 N sodium chloride
50 aqueous solution was 35.3 cp.

When 50 g of potassium sulfate was further added to this dispersion, the viscosity was reduced to 450 cp.

Example 19

55 To the separable flask used in Example 1 were added 2.3 g of a homopolymer of acryloyloxyethyltrimethylammonium chloride (the viscosity of its aqueous solution having a pure content of 0.5% being 20 cp at 25°C), 85 g of ammonium sulfate, 3.8 g of glycerin and 333.9 g of deionized water and dissolved, 34.7 g (75 mole%) of acrylamide, 31.5 g (18 mole%) of acryloyloxyethyltrimethylammonium chloride and 8.8 g (7 mole%) of acryloyloxyethyltrimethylammonium chloride were charged thereinto, heated to 45°C
60 and the air inside was displaced by nitrogen.

2.3 g of a 1% aqueous solution of 2,2'-azobis(2-amidinopropane) hydrochloride was added thereto, and the polymerization was conducted with stirring at 45°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

The viscosity of this product was 720 cp at 25°C, and the viscosity of the polymer at 0.5% in 3% sodium
65 sulfate aqueous solution was 65 cp.

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Example 20

To the separable flask used in Example 1 were added 7.5 g of a homopolymer of sodium acrylate (the viscosity of its aqueous solution of a pure content of 0.5% being 10 cp at 25°C), 42.5 g of ammonium sulfate, 42.5 g of diammonium hydrogenphosphate and 331.8 g of deionized water and dissolved, 75 g of acrylamide and, as a chain transfer agent, 0.75 g of isopropyl alcohol were charged, heated to 40°C, and the air inside was displaced by nitrogen.

0.75 g of a 1% aqueous solution of ammonium persulfate and 0.75 g of a 1% aqueous solution of sodium hydrogensulfite were added thereto as polymerization initiators, and the polymerization was conducted with stirring at 40°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

The viscosity of this product was 2300 cp at 25°C, and the viscosity of the polymer at 0.5% in 1 N sodium chloride aqueous solution was 40.2 cp.

Example 21

To the separable flask used in Example 1 were added 7.5 g of a homopolymer of sodium 2-acrylamido-2-methylpropanesulfonate (the viscosity at a pure content of 0.5% being 20 cp at 25°C), 100 g of ammonium sulfate and 292.5 g of deionized water and dissolved, then 75 g of acrylamide was charged thereto, heated to 45°C, and the air inside was displaced by nitrogen.

0.75 g of a 1% aqueous solution of ammonium persulfate and 0.75 g of a 1% aqueous solution of sodium hydrogensulfite were added thereto, and the polymerization was conducted with stirring at 45°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution. The viscosity of this product was 7500 cp at 25°C, and the viscosity of the polymer at 0.5% in 1 N sodium chloride aqueous solution was 65 cp.

When 25 g of diammonium hydrogenphosphate was further added to this dispersion, the viscosity was reduced to 550 cp.

Example 22

To the separable flask used in Example 1 were added 2.5 g of a homopolymer of sodium acrylate (the viscosity of its aqueous solution of a pure content of 0.5% being 10 cp at 25°C), 2.5 g of a homopolymer of sodium 2-acrylamido-2-methylpropanesulfonate (the viscosity of its aqueous solution of a pure content of 0.5% being 30 cp), 112.5 g of ammonium sulfate and 332.5 g of deionized water and dissolved, 43.6 g (90 mole%) of acrylamide and 6.4 g (10 mole%) of sodium acrylate were charged thereinto, heated to 45°C, and the air inside was displaced by nitrogen.

1.5 g of a 1% aqueous solution of 2,2'-azobis(2-amidinopropane) hydrochloride, and the polymerization was conducted with stirring at 45°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

The viscosity of this product was 3800 cp at 25°C, and the viscosity of the polymer at 0.5% in 1 N sodium chloride aqueous solution was 35.5 cp.

Example 23

To the separable flask used in Example 1 were added 7.5 g of a homopolymer of sodium 2-acrylamido-2-methylpropanesulfonate (the viscosity of its aqueous solution of a pure content of 0.5% being 19 cp at 25°C), 106.3 g of ammonium sulfate and 310.5 g of deionized water and dissolved, 51.5 g (90 mole%) of acrylamide, 23.5 g (10 more%) of sodium 2-acrylamido-2-methylpropanesulfonate and, as a chain transfer agent, 0.75 g of benzyl alcohol were charged thereinto, heated to 45°C, and the air inside was displaced by nitrogen.

2.3 g of a 1% aqueous solution of 2,2'-azobis(2-amidinopropane) hydrochloride was added thereto, and the polymerization was conducted with stirring at 45°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

The viscosity of this product was 1500 cp at 25°C, and the viscosity of the polymer at 0.5% in 1 N sodium chloride aqueous solution was 25 cp.

Example 24

To the separable flask used in Example 1 were added 7.5 g of a homopolymer of sodium acrylate (the viscosity of its aqueous solution of a pure content of 0.5% being 10 cp at 25°C), 51 g of ammonium sulfate, 34 g of diammonium hydrogenphosphate and 331.8 g of deionized water and dissolved, then 57.6 (90 more%) of acrylamide, 4.2 g (5 mole%) of sodium acrylate, 13, 2 g (5 mole%) of sodium 2-acrylamido-2-methylpropanesulfonate and, as a chain transfer agent, 0.75 g of isopropyl alcohol were charged thereinto, heated to 45°C, and the air inside was displaced by nitrogen.

1.5 g of a 1% aqueous solution of ammonium persulfate and 1.5 g of 1% aqueous solution of sodium hydrogensulfite were added thereto, and the polymerization was conducted with stirring at 45°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

The viscosity of this product was 1030 cp at 25°C, and the viscosity of the polymer at 0.5% in 1 N sodium chloride aqueous solution was 30 cp.

Example 25

To the separable flask used in Example 1 were added 3.8 g of a homopolymer of acryloyloxyethyltrimethylammonium chloride (the viscosity of its aqueous solution of a pure content of 0.5% being 20 cp at 25°C), 51 g of aluminum sulfate, 34 g of sodium sulfate and 336.2 g of deionized water and dissolved, then 75 g of acrylamide was charged thereinto, heated to 50°C, and the air inside was displaced by nitrogen.

1.5 g of a 1% aqueous solution of 2,2'-azobis(2-amidinopropane) hydrochloride was added thereto, and the polymerization was conducted with stirring at 50°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

The viscosity of this product was 4100 cp at 25°C, and the viscosity of the polymer at 0.5% in 1 N sodium chloride aqueous solution was 55 cp.

Example 26

To the separable flask used in Example 1 were added 3.8 g of a homopolymer of methacryloyloxyethyltrimethylammonium chloride (the viscosity of its aqueous solution of a pure content of 0.5% being 100 cp at 25°C), 106.3 g of ammonium sulfate and 314.9 g deionized water and dissolved, then 56.6 g (90 mole%) of acrylamide and 18.4 g (10 mole%) of methacryloyloxyethyltrimethylammonium chloride were charged thereinto, heated to 45°C, and the air inside was displaced by nitrogen.

1.5 g of a 1% aqueous solution of ammonium persulfate and 1.5 g of a 1% aqueous solution of sodium hydrogen-sulfite were added thereto, and the polymerization was conducted with stirring at 45°C for 10 hours to obtain a polymer in the form of fine particles dispersed in the aqueous salt solution.

The viscosity of this product was 2550 cp at 25°C, and the viscosity of the polymer at 0.5% in 1 N sodium chloride aqueous solution was 20.3 cp.

Comparative Example 1

To the separable flask used in Example 1 were added 112.5 g of ammonium sulfate and 337.5 g of deionized water and dissolved, then 35.1 g (90 more%) of acrylamide and 14.9 g (10 mole%) of acryloyloxy-ethyltrimethylbenzylammonium chloride were charged thereinto, heated to 50°C, and the air inside was displaced by nitrogen.

1.0 g of a 1% aqueous solution of 2,2'-azobis(2-amidinopropane) hydrochloride was added thereto, and the polymerization was conducted with stirring at 50°C for 10 hours to obtain a polymer in the form of dispersed particles of a particle diameter of 2—3 mm, but when the polymer to be co-present was not present as above, these particles, after one night's standing, stuck to each other to grow into a mass and did not disperse again.

Comparative Example 2

To the separable flask used in Example 1 were added 112.5 g of ammonium sulfate and 337.5 g of deionized water and dissolved 50 g of acrylamide was charged thereinto, heated to 40°C, and the air inside was displaced by nitrogen.

1 g of a 1% aqueous solution of ammonium persulfate and 1 g of a 1% aqueous solution of sodium hydrogensulfite were added thereto, and the polymerization was conducted with stirring at 40°C, but 10 minutes later, the viscosity is increased and the whole system became a mass.

Example 27

The products of this invention produced by the examples and a product produced by conventional aqueous solution polymerization were compared for the properties.

TABLE 1

Product Name	Concentration of the Polymer	Solution Viscosity ¹⁾	Product Viscosity
Example 1	10%	22.0 (cp)	500 (cp)
2	15	32.0	2400
3	10	20.0	1080
Aqueous Solution Polymerized Product ²⁾	10	20.0	Gel form and shows no flowability

1) The solution viscosity is the viscosity of the polymer at 0.5% in 1 N sodium chloride aqueous solution.

2) The monomer composition of the aqueous solution polymerized product was the same as in Examples 1 and 2.

Thus, those having the same molecular weight were obtained as flowable products having lower viscosity as compared with the aqueous solution polymerized product.

Example 28

- 5 The products of this invention produced in the examples and a commercially available powdered product were compared for the time to be completely dissolved in water.
(Dissolution was conducted by a magnetic stirrer to make an aqueous solution of 0.2% of the polymer).

TABLE 2

10	Product Name	Concentration of the Polymer	Solution Viscosity ¹⁾	Dissolution Time
15	Example 1	10%	22.0 (cp)	20 (min)
	2	15	32.0	20
	3	10	20.0	20
20	Powdered Product ²⁾	95	20.0	60

25 1) The solution viscosity is the viscosity of the polymer at 0.5% in 1 N sodium chloride aqueous solution.

2) The monomer composition of the powdered product was the same as in Examples 1 and 2.

Thus, it was found that the dissolution time is very rapid as compared with the powdered product.

30 The features disclosed in the foregoing description and in the following claims may, both separately and in any combination thereof, be material for realising the invention in diverse forms thereof.

Claims

35 1. A process for the production of a water-soluble polymer dispersion, which process comprises polymerizing a water-soluble monomer with stirring in an aqueous solution of at least one salt, in the presence of a dispersant.

2. A process according to Claim 1, wherein the salt and the salt concentration are such that the polymer is not dissolved and the dispersant is dissolved.

3. A process according to Claim 1 or 2, wherein the dispersant is a polyol.

40 4. A process according to Claim 3, wherein the polyol is one or a mixture of two or more of ethylene glycol, propylene glycol, glycerin, pentaerythritol and sorbitol.

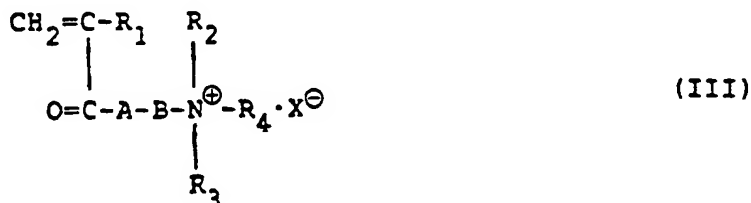
5. A process according to Claim 3, wherein the polyol is polyethylene glycol and/or polypropylene glycol having a molecular weight of up to 600.

6. A process according to Claim 1 or 2, wherein the dispersant is a polymer electrolyte.

45 7. A process according to Claim 6, wherein the dispersant is a polymer of an acrylic acid alkali metal salt and/or a 2-acrylamido-2-methylpropanesulfonic acid alkali metal salt or a copolymer containing 30 mole% or more thereof.

8. A process according to Claim 6, wherein the dispersant is a polymer of one or more cationic monomers of the formula (III) below or a copolymer containing 20 mole% or more thereof:

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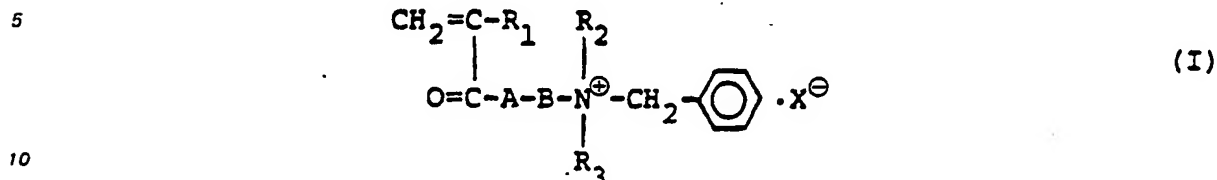


60

wherein R₁ is H or CH₃; R₂ and R₃ are each an alkyl group of 1—2 carbon atoms; R₄ is H or an alkyl group of 1—2 carbon atoms; A is an oxygen atom or NH; B is an alkylene group of 2—4 carbon atoms or a hydroxypropylene group; and X[−] is an anionic counterion.

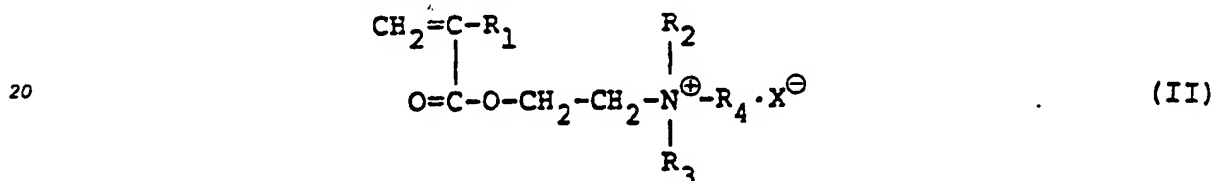
65 9. A process according to any one of the preceding claims, wherein 85 mole% or more of the water-soluble monomer is acrylamide.

10. A process according to any one of Claims 1 to 8, wherein the water-soluble monomer is a mixture of one or more cationic monomers of the formula (I) below and other monomer(s) copolymerizable therewith at a molar ratio in the range of 100:0 to 5:95:



wherein R₁ is H or CH₃; R₂ and R₃ are each an alkyl group of 1—3 carbon atoms; A is an oxygen atom or NH; B is an alkylene group of 2—4 carbon atoms or a hydroxypropylene group; and X⁻ is an anionic counterion.

11. A process according to any one of Claims 1 to 8, wherein the water-soluble monomer is a monomer mixture of one or more cationic monomers of the formula (II) below and (meth)-acrylamide, the monomer(s) of the formula (II) being up to 15 mole%:



wherein R₁ is H or CH₃; R₂ and R₃ are each an alkyl group of 1—3 carbon atoms; R₄ is H or an alkyl group or alkanol group of 1—3 carbon atoms; and X⁻ is an anionic counterion.

12. A process according to any one of Claims 1 to 8, wherein the water-soluble monomer is a monomer mixture of a (meth)acrylic acid alkali metal salt and (meth)acrylamide, the (meth)acrylic acid alkali metal salt being up to 15 mole%.

13. A process according to any one of Claims 1 to 8, wherein the water-soluble monomer is a monomer mixture of a 2-acrylamido-2-methylpropanesulfonic acid alkali metal salt and (meth)acrylamide, the 2-acrylamido-2-methylpropanesulfonic acid alkali metal salt being up to 15 mole%.

Patentansprüche

1. Verfahren zur Herstellung einer wasserlöslichen Polymerdispersion, gekennzeichnet durch Polymerisieren eines wasserlöslichen Monomers unter Rühren in einer wässrigen Lösung von wenigstens einem Salz, in Gegenwart eines Dispersionsmittels.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Salz und die Salzkonzentration derart sind, daß das Polymer nicht gelöst wird und das Dispersionsmittel gelöst wird.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Dispersionsmittel ein Polyol ist.

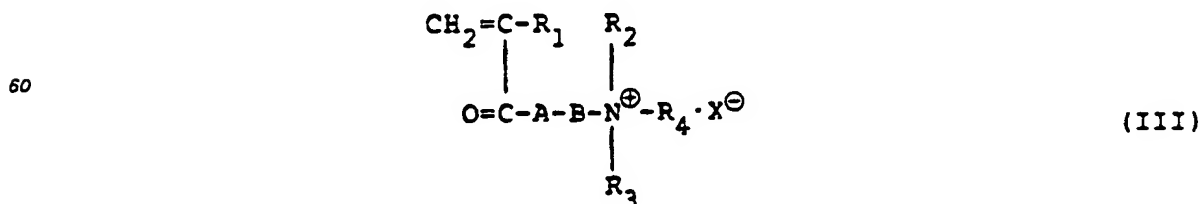
4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß das Polyol eine oder eine Gemisch von zwei oder mehre der folgenden Verbindungen ist: Ethylenglykol, Propylenglykol, Glycerin, Pentaerythrit und Sorbit.

5. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß das Polyol Polyethylenglykol und/oder Polypropylenglykol mit einem Molekulargewicht von bis zu 600 ist.

6. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Dispersionsmittel ein Polymerelektrolyt ist.

7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß das Dispersionsmittel ein Polymer eines Acrylsäure-Alkalimetallsalzes und/oder eines 2-Acrylamido-2-methylpropansulfonsäure-Alkalimetallsalzes oder ein Copolymer ist, das 30 Mol-% oder mehr davon enthält.

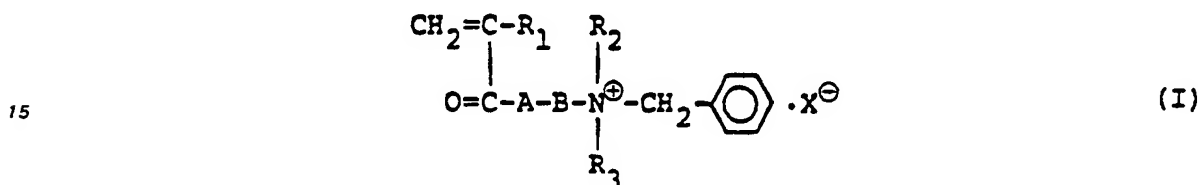
8. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß das Dispersionsmittel ein Polymer von einem oder mehreren kationischen Monomeren der Formel (III) unten oder in Copolymer ist, das 20 Mol-% oder mehr davon enthält:



wobei R_1 H oder CH_3 ist; R_2 und R_3 jeweils in eine Alkylgruppe mit 1 bis 2 Kohlenstoffatomen sind; R_4 H oder eine Alkylgruppe mit 1 bis 2 Kohlenstoffatomen ist; A ein Sauerstoffatom oder NH ist; B eine Alkylgruppe mit 2 bis 4 Kohlenstoffatomen oder eine Hydroxypropylengruppe ist; und X^- ein anionisches Gegenion ist.

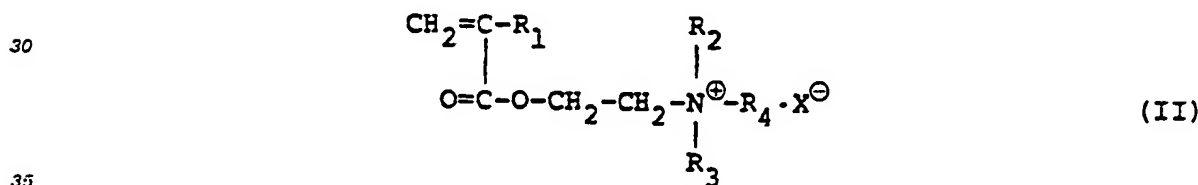
5 9. Verfahren nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß 85 Mol-% oder mehr des wasserlöslichen Monomers Acrylamid sind.

10 10. Verfahren nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß das wasserlösliche Monomer ein Gemisch von einem oder mehreren kationischen Monomeren der Formel (I) unten und anderen damit copolymerisierbaren Monomeren in einem Molverhältnis in Bereich von 100:0 bis 5:95 ist:



20 wobei R_1 H oder CH_3 ist; R_2 und R_3 jeweils in eine Alkylgruppe mit 1 bis 3 Kohlenstoffatomen sind; A ein Sauerstoffatom oder NH ist; B eine Alkylengruppe mit 2 bis 4 Kohlenstoffatomen oder ein Hydroxypropylengruppe ist; und X^- ein anionisches Gegenion ist.

25 11. Verfahren nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß das wasserlösliche Monomer ein Monomerengemisch von einem oder mehreren kationischen Monomeren der Formel (II) unten und (Meth)acrylamid ist, wobei das Monomer (die Monomeren) der Formel (II) bis zu 15 Mol-% ausmacht (ausmachen):



30 wobei R_1 H oder CH_3 ist; R_2 und R_3 jeweils in eine Alkylgruppe mit 1 bis 3 Kohlenstoffatomen sind; R_4 H oder eine Alkylgruppe oder Alkanolgruppe mit 1 bis 3 Kohlenstoffatomen ist; und X^- ein anionisches Gegenion ist.

40 12. Verfahren nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß das wasserlösliche Monomer ein Monomerengemisch aus einem (Meth)acrylsäure-Alkalimetallsalz und (Meth)acrylamid ist, wobei das (Meth)acrylsäure-Alkalimetallsalz bis zu 15 Mol-% ausmacht.

45 13. Verfahren nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß das wasserlösliche Monomer ein Monomerengemisch aus einem 2-Acrylamido 2-methylpropansulfonsäure-Alkalimetallsalz und (Meth)acrylamid ist, wobei das 2-Acrylamido-2-methylpropansulfonsäure-Alkalimetallsalz bis zu 15 Mol-% ausmacht.

Revendications

50 1. Procédé de préparation d'une dispersion d'un polymère soluble dans l'eau qui comprend la polymérisation d'un monomère soluble dans l'eau sous agitation dans une solution aqueuse d'au moins un sel, en présence d'un dispersant.

55 2. Procédé selon la revendication 1, dans lequel le sel et la concentration du sel sont tels que le polymère n'est pas dissous et le dispersant est dissous.

3. Procédé selon la revendication 1 ou 2, dans lequel le dispersant est un polyol.

4. Procédé selon la revendication 3, dans lequel le polyol est un polyol ou un mélange de deux ou plusieurs polyols parmi l'éthylèneglycol, le propylèneglycol, la glycérine, le pentaérythritol et le sorbitol.

60 5. Procédé selon la revendication 3, dans lequel le polyol est un poly(éthylèneglycol) et/ou un poly(propylèneglycol) ayant une masse moléculaire allant jusqu'à 600.

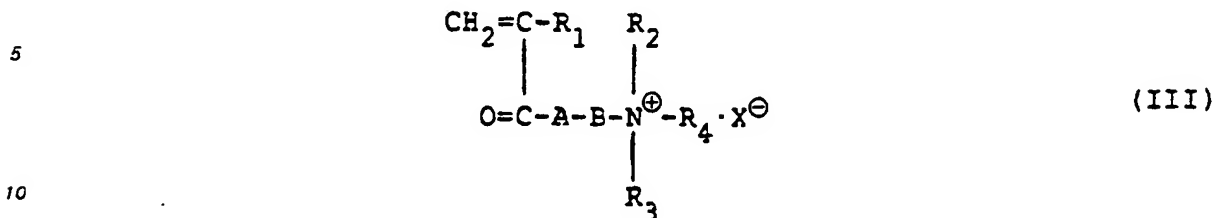
6. Procédé selon la revendication 1 ou 2, dans lequel le dispersant est un électrolyte polymérique.

7. Procédé selon la revendication 6, dans lequel le dispersant est un polymère d'un sel de métal alcalin de l'acide acrylique et/ou d'un sel de métal alcalin de l'acide 2-acrylamido-2-méthylpropanesulfonique ou un copolymère contenant 30% en mole ou plus de celui-ci.

65 8. Procédé selon la revendication 6, dans lequel le dispersant est un polymère d'un ou plusieurs

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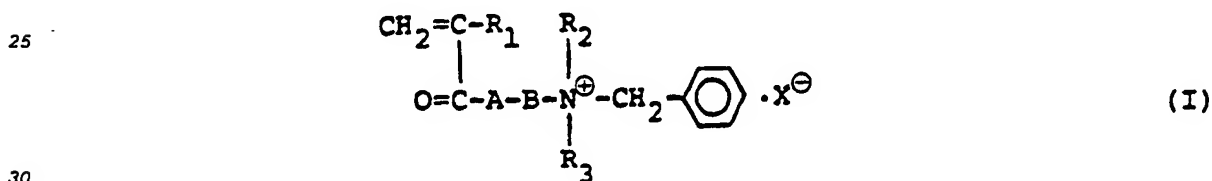
monomères cationiques de formule (III) ci-dessous ou un copolymère contenant 20% en mole ou plus de celui-ci:



où R_1 représente H ou CH_3 ; R_2 et R_3 représentent chacun un groupe alkyle avec 1—2 atomes de carbone; R_4 représente H ou un groupe alkyle avec 1—2 atomes de carbone; A représente un atome d'oxygène ou NH; B représente un groupe alkylène avec 2—4 atomes de carbone ou un groupe hydroxypropylène; et X^- est un contre-ion anionique.

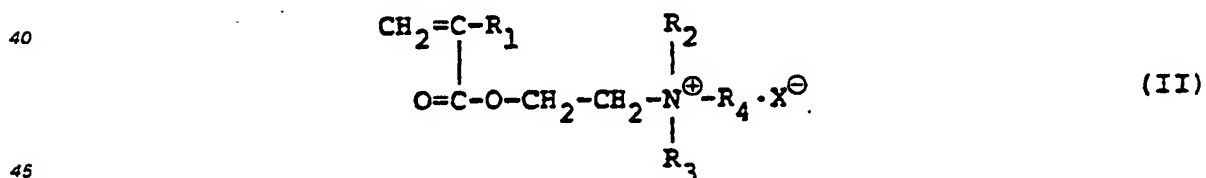
9. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'acrylamide représente 85% en mole ou plus du monomère soluble dans l'eau.

10. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel le monomère soluble dans l'eau est un mélange d'un ou plusieurs monomères cationiques de formule (I) ci-dessous et d'autre(s) monomère(s) copolymérisable(s) avec eux dans un rapport molaire compris dans l'intervalle allant de 100:0 à 5:95.



où R_1 représente H ou CH_3 ; R_2 et R_3 représentent chacun un groupe alkyle avec 1—3 atomes de carbone; A représente un atome d'oxygène ou NH; B représente un groupe alkylène avec 2—4 atomes de carbone ou un groupe hydroxypropylène; et X^- est un contre-ion anionique.

11. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel le monomère soluble dans l'eau est un mélange monomère d'un ou plusieurs monomères cationiques de formule (II) ci-dessous et de (méth)acrylamide, le(s) monomère(s) de formule (II) allant jusqu'à 15% en mole:



où R_1 représente H ou CH_3 ; R_2 et R_3 représentent chacun un groupe alkyle avec 1—3 atomes de carbone; R_4 représente H ou un groupe alkyle ou un groupe alcool ayant 1—3 atomes de carbone; et X^- représente un contre-ion anionique.

12. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel le monomère soluble dans l'eau est un mélange monomères d'un sel de métal alcalin de l'acide (méth)acrylique et de (méth)acrylamide, le sel de métal alcalin de l'acide (méth)acrylique allant jusqu'à 15% en mole.

13. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel le monomère soluble dans l'eau est un mélange monomères d'un sel de métal alcalin de l'acide 2-acrylamido-2-méthylpropanesulfonique et de (méth)acrylamide, le sel de métal alcalin de l'acide 2-acrylamido-2-méthylpropanesulfonique allant jusqu'à 15% en mole.

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